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### Effect of boron powder purity on superconducting properties of MgB<sub>2</sub>

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# **Effect of Boron powder purity on superconducting properties of MgB<sub>2</sub>**

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## **Abstract**

The effect of the properties of starting Boron powders on the superconducting properties of MgB<sub>2</sub> has been studied. The 92% and 96% powders demonstrate lower surface reactivity and larger particle size than the 99% Boron powder as can be seen from BET and SEM results, indicating that the low purity powders cannot be used to archive the same superconducting properties as those of samples made from pure 99% B powder. However, the purity of 92% and 96% Boron powders can be improved by using a simple chemical process, leading to enhanced magnetic critical current densities J<sub>c</sub>. From XRD measurement, oxide impurity has been observed, which might be originated from the B<sub>2</sub>O<sub>3</sub> phase in the Boron powders. In order to get high performance MgB<sub>2</sub>, it is obviously important to control the phase composition and microstructure of amorphous boron starting powders and solid reaction conditions.

## 1. Introduction

Since the discovery of the superconductivity of  $\text{MgB}_2$  [1], there has been a considerable amount of research undertaken to understand the enhancement of  $J_c$  performance by means of dopants and nano-particle additions [2-7]. On the other hand, the properties of the starting Boron powders, such as purity, particle size etc., may also play an important role in determining the superconducting properties of  $\text{MgB}_2$ . It has been reported that samples made from crystalline boron powders have around an order of magnitude lower  $J_c$  than samples made from amorphous precursors [9]. Gas phase plasma methods for powder production have been used to promote intimate mixing of the doping components on an atomic scale in the initial Boron powder production, both the grain size and the precipitate size have been reported to be smaller [8]. It has also been found that the enhancement in  $J_c$  by mixing  $\text{MgB}_2$  with  $(\text{MgH}_2+2\text{B})$  is due to the optimization of densification by  $\text{MgB}_2$  addition and improvement in grain coupling depending on the phase formation of  $\text{MgB}_2$  from  $(\text{MgH}_2+2\text{B})$  [10]. In another study, elementary boron was obtained via acid leaching process, after reacting  $\text{B}_2\text{O}_3$  and Mg in an argon atmosphere at 800 °C, EDX results revealed that the powder obtained from the reaction was boron of 92% purity with magnesium as the major impurity [11]. The effect of B powder purity on  $J_c$  and  $T_c$  has also been found to be noticeable [12]. Currently, in order to achieve the highest  $J_c$ , high purity amorphous B powders (99%) were used. However, in practical applications, the cost of the materials must be considered. The pure (99%) amorphous boron powder is about 10 times more expensive than the low-grade (96%, 92%) amorphous powders. If the 92% or 96% Boron powders can be used to make  $\text{MgB}_2$ , the material cost could be decreased significantly. In this work, we try to purify the low-

grade amorphous boron powders using an acid leaching process, study the effects of Boron powder purity and process parameters on the superconducting properties of  $\text{MgB}_2$ . We also investigate the effect of intrinsic impurities in  $\text{MgB}_2$  on the superconducting properties, which will give another window to investigate the doping process for  $\text{MgB}_2$ .

## **2. Experiment details**

### **2.1 Purify low –grade amorphous boron**

The mixture of 5g low–grade Boron power and 10mL ethanol was ball milled in a Tungsten carbide jar for 30mins, put into the solution of concentrated hydrochloric acid (50mL) and DI water (50mL) for 60mins, and boiled slowly on a hotplate with magnetic stirring, then cooled to room temperature. The sample was filtered with centrifugal separator, washed by DI water with swing motor and filtered again with centrifugal Separator, finally the sample was dried in vacuum furnace at 110 °C for 12 hours.

### **2.2 Prepare boron powder with different purities**

Boron powders of different purities (amorphous, irregular shape, 99%, 96%, 92%) and purified (96%, 92%) Boron powders made by simple chemical process were measured by Scanning Electron Microscopy (SEM), Electron Dispersive Analysis (EDS) and Brunauer Emmett Teller (BET). The results will be discussed in the next section with the effect of process parameters on the  $\text{MgB}_2$  superconducting properties.

### **2.3 Prepare of $\text{MgB}_2$ with B powders**

MgB<sub>2</sub> samples were prepared by reacting Mg and B using solid state reaction using crystalline magnesium powder (99.8%, 325 mesh) and five different types of boron powders (pure 99%, original 96%, original 92%, purified 96%, purified 92%, the MgB<sub>2</sub> samples are named after these abbreviations). Mg and B were mixed in the atom ratio of 1:2, followed by hand milling (above 30 minutes). The mixture powder was then pressed into pellets about 13 mm in diameter and 3 mm in thickness using a hydraulic press with an applied load of 8 tones. The pellets were placed inside a tubular furnace and sintered at different temperatures (700 °C for 30 minutes, 3 hours, 6 hours, 825 °C for 30 minutes, 3 hours, respectively) under the protection of a high purity argon atmosphere. The heating rate is 10 °C/min, cooling down to room temperature naturally. The pellets were cut into small bar shaped pieces with a dimension of 2×2×3 mm<sup>3</sup>.

#### 2.4 Measurements for MgB<sub>2</sub>

X-ray diffraction in the  $\theta$  -  $2\theta$  step-scanning mode with 0.02° increments, 2 degrees/min were recorded in a Philips PW1730 diffract meter with a Cu-K $\alpha$  radiation source. In order to observe uniformity of grain size, SEM image pictures have been taken. The superconducting transition temperature ( $T_c$ ) was obtained using a commercial Quantum Design Magnetic Properties Measurement System (MPMS) by first cooling the sample in zero field and then measuring the magnetic moment as the sample was warmed up in field. Magnetizations hysteresis loops were performed on a commercial Quantum Design Physical Properties Measurement System (PPMS) with the magnetic field applied parallel to the longest dimension of the sample. Magnetic critical current density  $J_c$  was estimated based on the Bean's model.

### 3. Results and discussion

Table 1 shows the EDS results for the purity of the B powders studied. It can be seen from the table that after leaching the purity of the 92% boron has been increased to above 95%, while the purity of 96% powder was only slightly increased to 96.6%. The two main impurities in the starting powders are Mg and Oxygen, for the 92% Boron both Mg and Oxygen can be greatly removed after leaching (7.89 Atom% to 4.03 Atom%, and 1.83 Atom% to 0.68 Atom% for Oxygen and Mg, respectively). However, the 96% Boron powder is quite stable (2.89 Atom% to 3.04 Atom%, and 0.38 Atom% to 0.24 Atom% for Oxygen and Mg, respectively). As the Oxygen impurities are mainly from  $B_2O_3$  in the starting powders, we can see that  $B_2O_3$  can be removed by ethanol.

Figure 1 shows the BET results for the specific surface area of different B powders. The 99% B powder has a very high specific surface area ( $31.5 \text{ m}^2/\text{g}$ ). The leaching process shows little effect on the specific surface area (from  $12.94 \text{ m}^2/\text{g}$  to  $13.51 \text{ m}^2/\text{g}$ , and from  $10.84 \text{ m}^2/\text{g}$  to  $10.44 \text{ m}^2/\text{g}$ ).

SEM images for the powders are shown in Figure 2. As can be seen from the pictures, the 99% boron powders show smaller grain size and better grain homogeneity than the impure and purified powders. The particle sizes of 92% and 96% boron powders are not changed by the leaching process.

The X-ray diffraction patterns for  $\text{MgB}_2$  samples sintered at different conditions with 99%, 96% and purified 92% starting Boron powders are shown in Figure 3a, 3b and 3c, respectively. As can be seen from Figure 3a, no remnant Mg is observed for the 99% samples sintered at 700 °C for only 30 minutes, indicating that the boron powder has reacted completely with Mg. However, for the purified samples, remnant Mg is always observed event at the highest sintering temperature and longest sintering time, as can be seen from Figure 3b and 3c. The diffraction peak of MgO is higher for longer sintering time process, this is because the Argon protecting atmosphere is not kept good enough for longer sintering time, the longer the sintering time, the higher risk of oxidation, which is in agreement with the reported results [9].

The critical current densities as a function of the magnetic field for  $\text{MgB}_2$  samples (purified 92% and purified 96%) sintered at different conditions are shown in Figure 4a and 4b, respectively. For purified 92%, the  $J_c(H)$  performance is almost independent of the sintering conditions. While for purified 96%, the  $J_c(H)$  performance is improved with higher sintering temperature and/or longer sintering time. Plotted in Figure 5 are the  $J_c(H)$  curves for  $\text{MgB}_2$  samples (original 96%, purified 96%, purified 92% and pure 99%). It can be seen from the figure that the purifying process has a strong effect on the superconducting properties of  $\text{MgB}_2$  superconductors. At 20K, compared to the original 96% sample, the purified 96% sample shows enhanced  $J_c(H)$  performance at high field closed to the irreversibility field, and the irreversibility field is increased from 4.1T to 4.8T (using  $J_c=100 \text{ A/cm}^2$  as the criterion for the irreversibility field). What is more interesting is the result of the purified 92% sample, its critical current density is much



better than that of the purified 96% samples. The reason is probably that the grain homogeneity of the purified 96% is not as good as that of the purified 92% sample, as can be seen from the SEM pictures shown in Figure 3. The critical current density of the purified 92% sample is even better than that of the pure 99% sample at high field close to the irreversibility field, and therefore slightly increased the irreversibility field. Compared to the pure 99% sample, the critical current density of the purified 92% sample decreases slightly slower with increasing magnetic field, indicating that some of the remaining impurities in the purified 92% sample might act as pinning centers. However, in the wide magnetic field range (below 4.5T), the critical current density of the purified 92% sample is obviously lower than that of the pure 99% sample. From the XRD, SEM, BET, and EDS results, we can see that the purified powder still demonstrate more oxide impurities, lower surface reactivity, less uniform grain distributions, and larger grain size. In order to use the low-grade Boron powders to achieve high performance  $\text{MgB}_2$  samples, these properties must be improved, which will be our tasks in forthcoming works.

#### **4. Summary**

In summary, we have shown that the purity of starting boron powders are important in determining the  $J_c(H)$  performance of  $\text{MgB}_2$  sample, the purer the starting boron powders, the better the  $J_c(H)$  performance. We have purified 92% and 96% boron powders using a simple chemical leaching process, resulting in enhanced  $J_c(H)$  performance. However, compared to the pure 99% powder, the purified powders still show more oxide impurities, lower surface reactivity, less uniform grain distributions, and larger grain size, further

works are needed in order to use the 92% or 96% powders to make  $\text{MgB}_2$  wires for industrial applications.

### Acknowledgements

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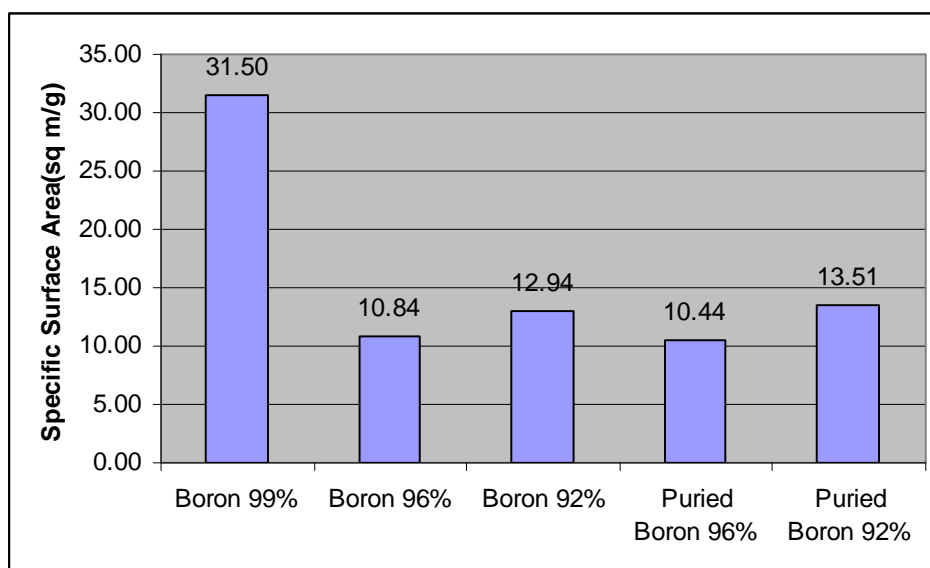
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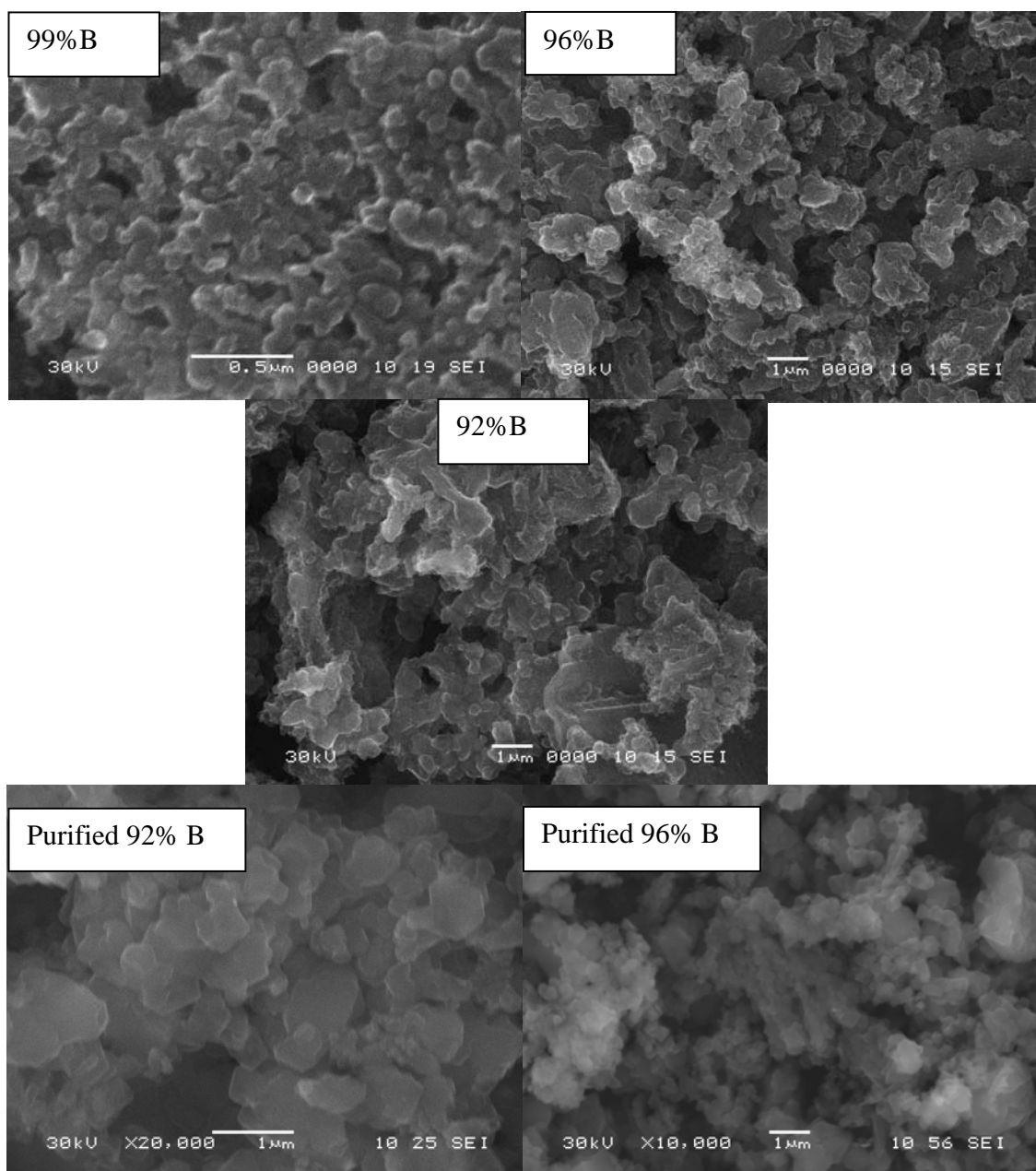
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	Atom%											
	B	O	F	Mg	Al	Si	Fe	Cu	Na	K	W	Ca
96% Boron	96.38	2.89	0.16	0.38	0.02	0.05	0.01	0.02	0.01	0.05		0.01
92% Boron	90.06	7.89		1.83	0.06	0.07		0.06				0.03
99% Boron	98.24	1.74				0.02		0.02				0.01
Purified92%	95.22	4.03		0.68		0.02		0.02			0.02	
Purified96%	96.64	3.04		0.24		0.02		0.02			0.02	

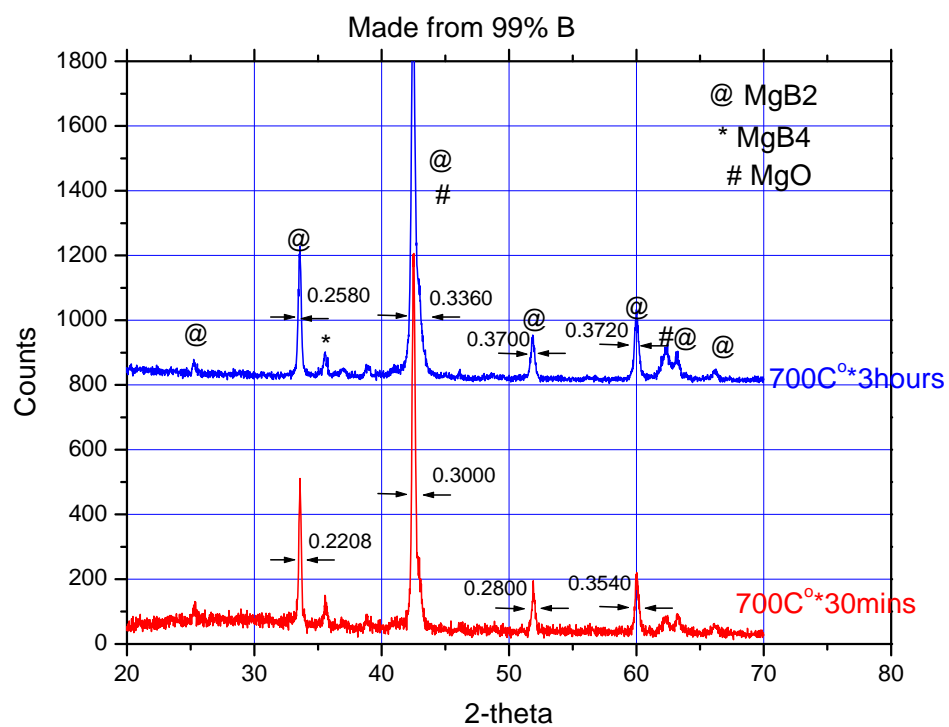
**Table 1.** EDS results for the purity of different B powders.



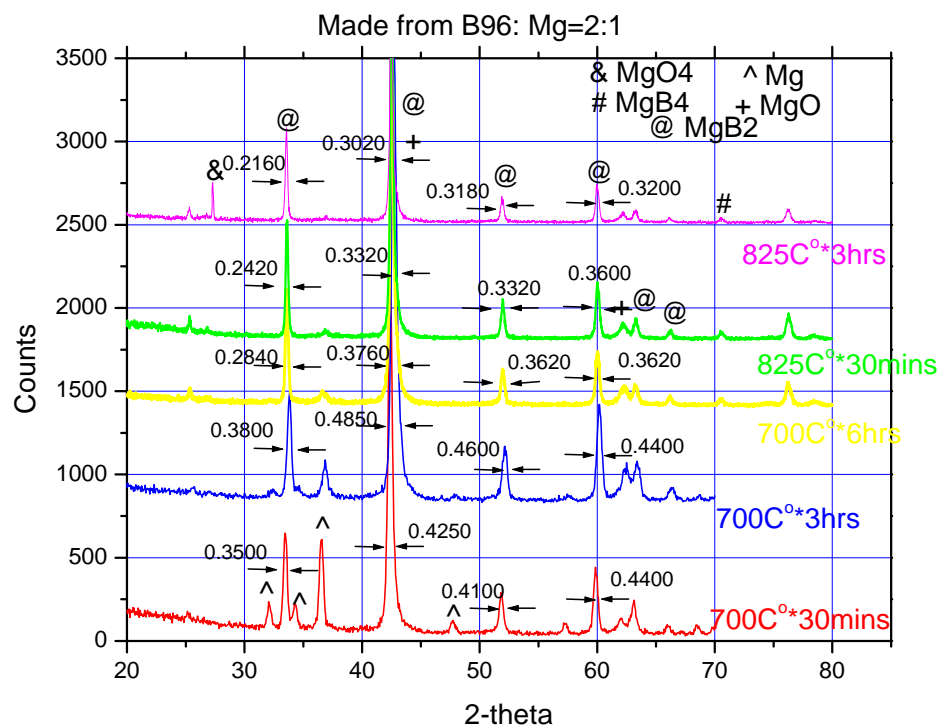
**Figure1.** BET results for different B powders



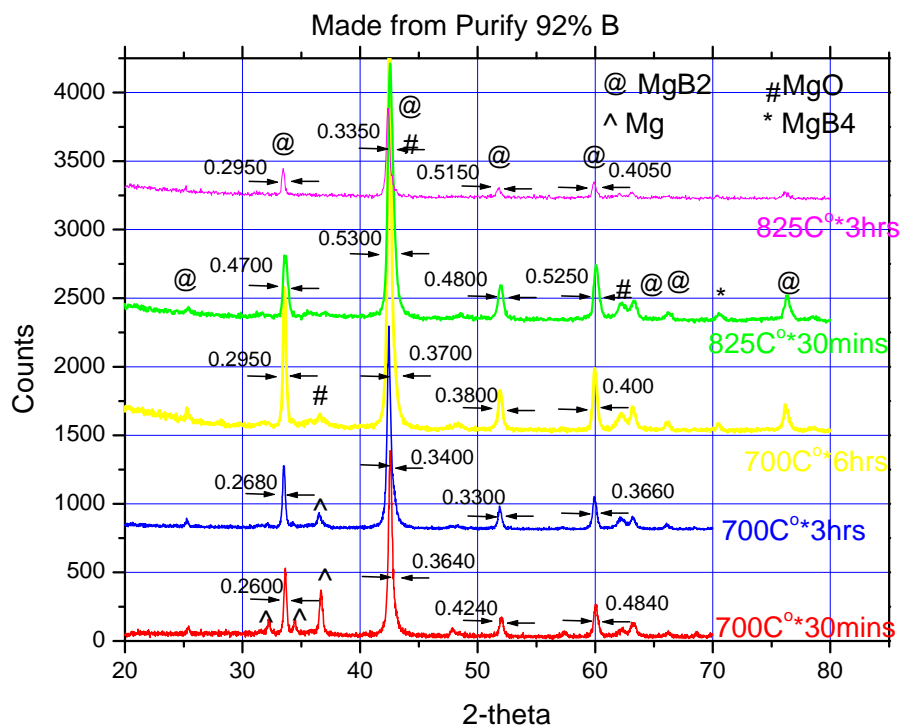
**Figure 2.** SEM images of different Boron powders



**Figure 3a.** X-ray powder diffraction patterns of MgB<sub>2</sub> samples made from pure 99% B powder

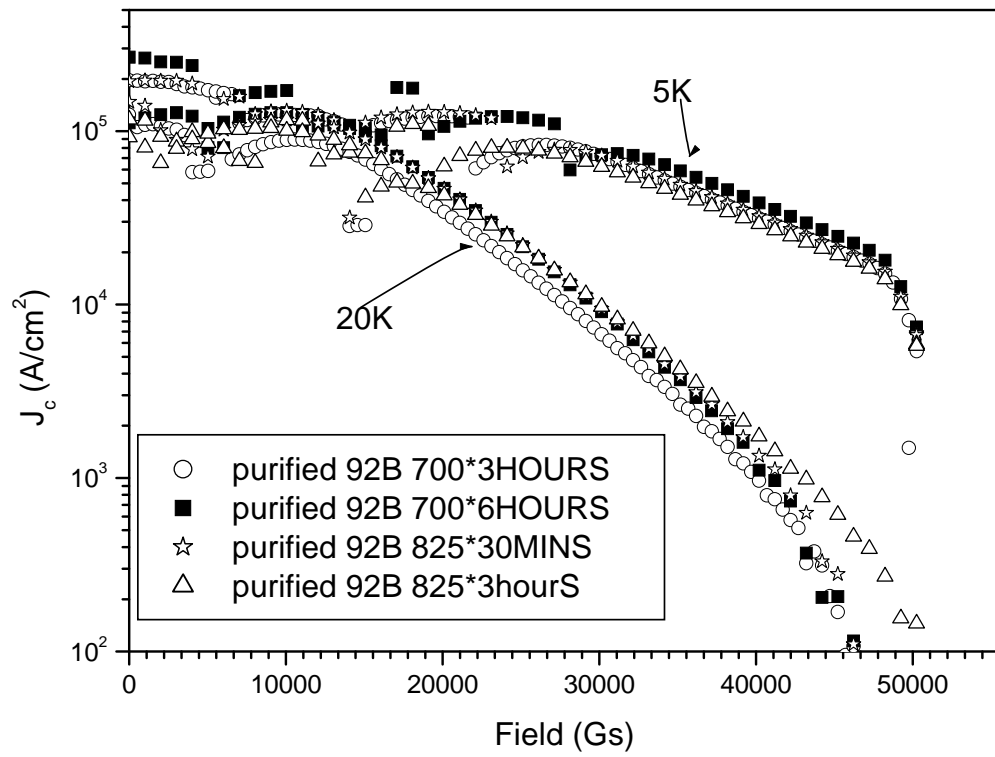


**Figure 3b.** X-ray powder diffraction patterns of MgB<sub>2</sub> samples made from 96% B powder

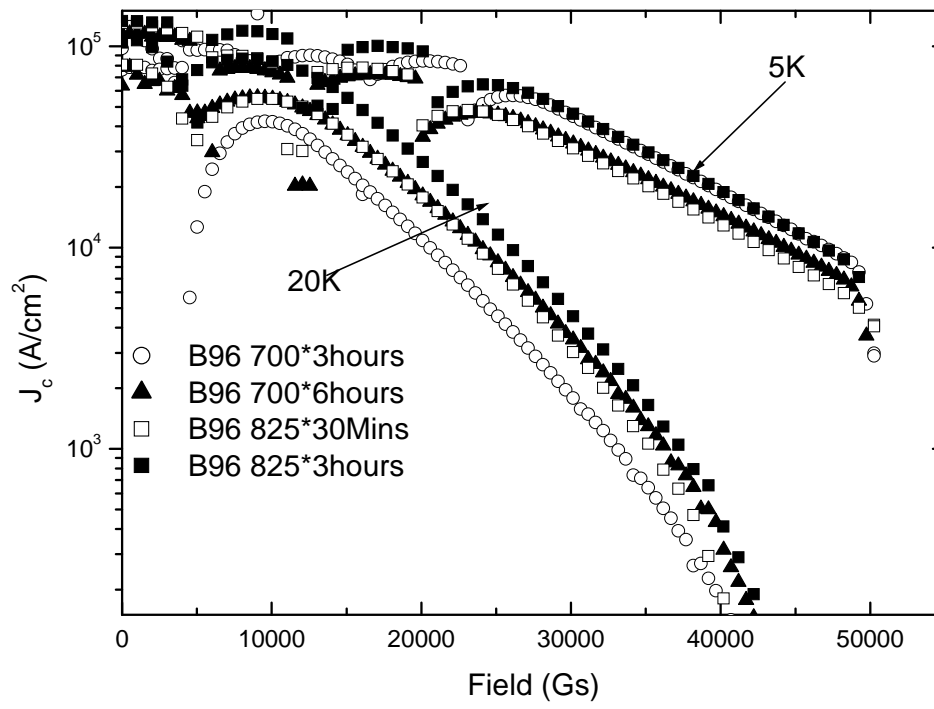


**Figure 3c.** X-ray powder diffraction patterns of MgB<sub>2</sub> samples made from purified 92% B powder

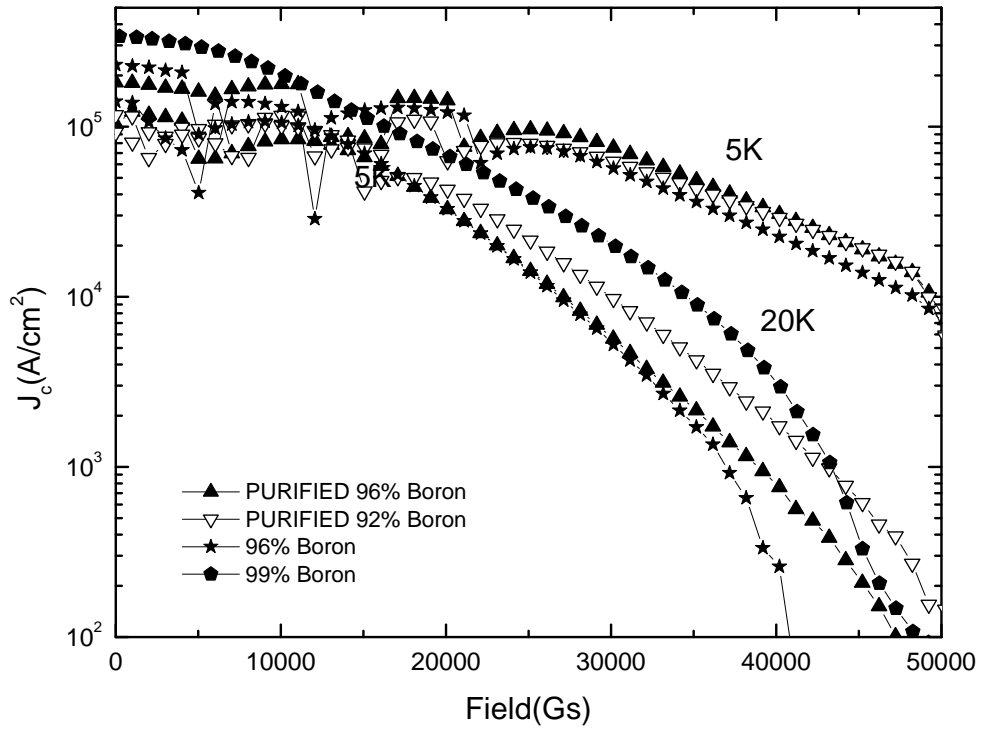




**Figure 4a.**  $J_c$  of samples made from purified 92% B powder



**Figure 4b.**  $J_c$  of samples made from 96% B powder



**Figure 5.**  $J_c$  of samples made from different B powder